# The use of aliphatic aldehydes for the synthesis of 4-alkyl-6-amino-3,5-dicyanopyridine-2(1*H*)-thiones

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The condensation of aliphatic aldehydes with malononitrile and cyanothioacetamide gives 4-alkyl-2,6-diamino-3,5-dicyano-4*H*-thiopyrans which recyclize into 4-alkyl-6-amino-3,5-dicyanopyridine-2(1*H*)-thiones. The latter are easily *S*-alkylated with α-haloacetonitriles and α-haloacetophenones.

**Key words:** 4-alkyl-2,6-diamino-3,5-dicyano-4*H*-thiopyrans, 4-alkyl-6-amino-3,5-dicyanopyridine-2(1*H*)-thiones, recyclization.

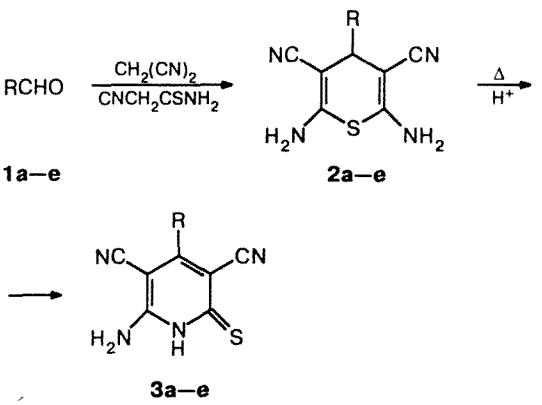
The synthesis of substituted pyridinethiones is a rapidly developing area in heterocyclic chemistry. Of special interest are 3-cyanopyridine-2(1*H*)-thiones,[1,2] which have a broad spectrum of biological activity and are convenient starting compounds to construct new annelated systems.

Aldehydes are used successfully in the syntheses of substituted 3-cyanopyridine-2(1*H*)-thiones.[1,2] We have recently reported[3] the possibility to obtain 4,6-dialkyl-3-cyanopyridine-2(1*H*)-thiones by converting aliphatic aldehydes into α,β-unsaturated ketones followed by condensation of the latter with cyanothioacetamide (CTA). In addition, it was shown[4–8] that the interaction of α,β-unsaturated nitriles with CTA resulted in various 6-amino-4-aryl(hetaryl)-3,5-dicyanopyridine-2(1*H*)-thiones.

In a continuation of our studies of the synthetic application of aldehydes we describe a new method for the synthesis of 4-alkyl-6-amino-3,5-dicyanopyridine-2(1*H*)-thiones.

When aliphatic aldehydes interact with malononitrile, the reaction does not stop at the stage of the formation of 2-alkyl-1,1-dicyanoethylene. It was noted[9] that reactions with compounds having an active methylene group are characteristic of alkylidenemalononitriles (addition, di- and codimerization). To avoid these processes when obtaining 4-alkyl-6-amino-3,5-dicyanopyridine-2(1*H*)-thiones (**3a—e**), a three-component condensation of aldehyde (**1a—e**), malononitrile, and CTA in ethanol was used in the presence of an organic base (Scheme 1). It can be supposed that the first stage of the process gives 2-alkyl-1,1-dicyanoethylene, whose direct interaction with CTA (according to the Michael reaction) results in 4-alkyl-2,6-diamino-3,5-dicyano-4*H*-thiopyrans (**2a—e**). When heated in ethanol, the latter undergo recyclization (accompanied by loss of molecular hydrogen) to give pyridine-2(1*H*)-thiones **3a—e** which are isolated by acidifying the solution with dilute hydrochloric acid.

**Scheme 1**




R = Pr (**a**), Pr$^i$ (**b**), Bu (**c**), Bu$^i$ (**d**), *n*-$C_7H_{15}$ (**e**)

Thiopyrans **2a—e** and pyridine-2(1*H*)-thiones **3a—e** are storage-stable crystalline compounds, colorless and yellow, respectively. The structures of these compounds were confirmed by spectroscopic methods (Tables 1—4) and chemical transformations (Scheme 2). Compounds **3a—e**, like their numerous analogs substituted at the pyridine ring,[1–8] exist in the thione tautomeric form. The IR spectra of compounds **2a—e** and **3a—e** exhibit intense absorption bands of the CN group in a 2190—2230 $cm^{-1}$ range and absorption bands of medium intensity of the CS group at 1150—1200 $cm^{-1}$ (for **3a—e**). A typical singlet for two $NH_2$ groups is registered in the $^1H$ NMR spectra of thiopyrans **2a—e** in a 6.71—6.81 ppm range. The $^1H$ NMR spectra of pyridinethiones

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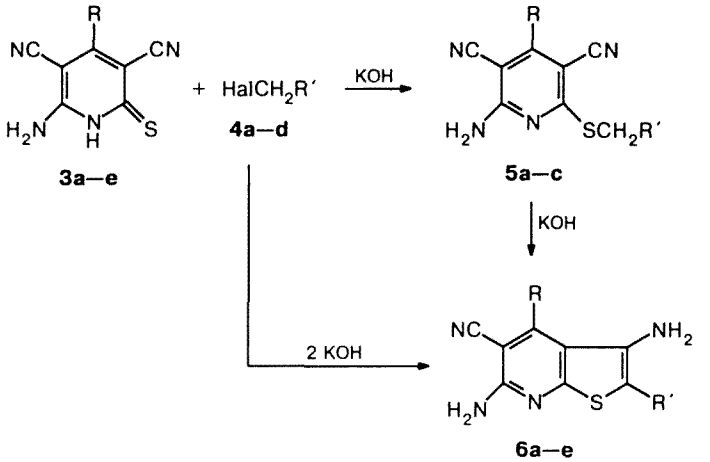
**Scheme 2**




**4a:** Hal = Cl, R′ = CN;
**4b:** Hal = Br, R′ = $COC_6H_5$;
**4c:** Hal = Br, R′ = $COC_6H_4Br$-*p*;
**4d:** Hal = Br, R′ = $COC_6H_4NO_2$-*p*;
**5a:** R = Pr, R′ = $COC_6H_4$—*p*-$NO_2$;
**5b:** R = Bu$^i$, R′ = CN;
**5c:** R = Bu$^i$, R′ = $COC_6H_4$—*p*-$NO_2$;
**6a:** R = Bu, R′ = $COC_6H_4$—*p*-Br;
**6b:** R = Bu, R′ = $COC_6H_4$—*p*-$NO_2$;
**6c:** R = Bu, R′ = CN;
**6d:** R = Bu$^i$, R′ = $COC_6H_5$;
**6e:** R = *n*-$C_7H_{15}$, R′ = $COC_6H_5$

**Table 1.** Characteristics of 4-alkyl-2,6-diamino-3,5-dicyano-4*H*-thiopyrans **2a—e**

| Compound | Yield (%) | M.p./°C | Found / Calculated (%) | | | | Molecular formula |
|---|---|---|---|---|---|---|---|
| | | | C | H | N | S | |
| **2a** | 55 | 168—170 | 54.48<br>54.52 | 5.51<br>5.49 | 25.40<br>25.44 | 14.52<br>14.56 | $C_{10}H_{12}N_4S$ |
| **2b** | 65 | 203—204 | 54.57<br>54.52 | 5.43<br>5.49 | 25.52<br>25.44 | 14.59<br>14.56 | $C_{10}H_{12}N_4S$ |
| **2c** | 40 | 98—100 | 56.42<br>56.38 | 6.04<br>6.02 | 23.90<br>23.91 | 13.65<br>13.68 | $C_{11}H_{14}N_4S$ |
| **2d** | 70 | 205—207 | 56.35<br>56.38 | 6.01<br>6.20 | 23.94<br>23.91 | 13.71<br>13.68 | $C_{11}H_{14}N_4S$ |
| **2e** | 40 | 168—170 | 60.80<br>60.83 | 7.30<br>7.29 | 20.26<br>20.27 | 11.62<br>11.60 | $C_{14}H_{20}N_4S$ |

**3a—e** exhibit a broadened singlet for the NH group in a 12.88—12.9 ppm range and a broadened singlet for the $NH_2$ group in a 7.8—7.9 ppm range. The UV spectra of compounds **3a—e** are characterized by the presence of four absorption peaks.

In the presence of an equimolar amount of aqueous KOH, thiones **3a—e** are easily alkylated at the sulfur atom with halides (**4a,d**) in solution in DMF (or ethanol) to give 4-alkyl-6-amino-3,5-dicyano-2-($R^1$-methylthio)pyridines (**5a—c**), whose structures are confirmed by the spectral data (Tables 5, 6). The absorption band of the CN group is present in the IR spectra of these compounds in the 2220—2270 $cm^{-1}$ range. The appearance of a singlet for the protons of the $SCH_2$ group in the 4.28—4.95 ppm range is a characteristic feature of the $^1H$ NMR spectra of pyridines **5a—c**.

4-Alkyl-3,6-diamino-5-cyanothieno[2,3-*b*]pyridines (**6a—e**) functionalized at position 2 were obtained in one step without prior synthesis of pyridines **5** by the interaction of thiones **3** with halides (**4a—d**) in the presence of an excess of KOH in DMF (or ethanol) at 20 °C (procedure *A*). In accordance with general regularities,[10] compounds **6a—e** can also be synthesized by the Thorpe—Ziegler cyclization of pyridine **5** (see Scheme 2) under the action of excess KOH in DMF (or ethanol) (procedure *B*). The structures of thieno[2,3-*b*]pyridines **6a—e** were confirmed by spectroscopic studies (see Tables 5 and 6).

**Table 2.** Spectral characteristics of 4-alkyl-2,6-diamino-3,5-dicyano-4*H*-thiopyrans **2a—e**

| Compound | IR, $\nu$CN/cm$^{-1}$ | Mass spectrum, $m/z$ ($I_{rel}$ (%)) | $^1$H NMR, $\delta$ |
|---|---|---|---|
| **2a** | 2195 | 220 (7.0), 179 (19.0), 178 (41.2), 177 (100.0), 160 (13.7), 154 (5.9), 143 (18.9), 118 (14.0), 60 (13.2) | 0.9 (t, 3 H, $CH_3$); 1.33 (m, 2 H, $CH_2$); 1.45 (t, 2 H, $\underline{CH_2}CH_3$); 2.95 (t, H, H(4)); 6.8 (s, 4 H, $NH_2$) |
| **2b** | 2195 | 178 (100.0), 160 (23.9), 150 (20.5), 143 (39.8), 123 (25.0), 90 (38.7), 80 (25.0), 70 (25.0), 60 (96.6) | 0.89 (d, 6 H, 2 $CH_3$); 1.8 (m, H, CH); 2.67 (d, H, H(4)); 6.8 (s, 4 H, $NH_2$) |
| **2c** | 2190 | 234 (45.5), 179 (100.0), 160 (65.5), 143 (78.0), 118 (61.9), 100 (36.0), 91 (25.5), 60 (63.7) | 0.86 (t, 3 H, $CH_3$); 1.29 (m, 4 H, $(CH_2)_2$); 1.48 (t, 2 H, $\underline{CH_2}CH_3$); 2.93 (t, H, H(4)); 6.79 (s, 4 H, $NH_2$) |
| **2d** | 2198 | 234 (14.3), 179 (100.0), 168 (14.3), 160 (28.6), 150 (21.4), 143 (47.1), 118 (42.9), 60 (50.0) | 0.89 (d, 6 H, 2 $CH_3$); 1.34 (t, 2 H, $CH_2$); 1.65 (m, H, CH); 2.96 (t, H, H(4)); 6.81 (s, 4 H, $NH_2$) |
| **2e** | 2196 | 276 (20.0), 205 (22.5), 173 (100.0), 155 (25.0), 134 (31.3), 113 (27.5), 95 (30.0) | 0.85 (t, 3 H, $CH_3$); 1.25 (s, 10 H, $(CH_2)_5$); 1.47 (t, 2 H, $\underline{CH_2}CH_3$); 2.95 (t, H, H(4)); 6.81 (s, 4 H, $NH_2$) |

**Table 3.** Characteristics of 4-alkyl-6-amino-3,5-dicyanopyridine-2(1*H*)-thiones **3a—e**

| Compound | Yield (%) | M.p./°C | Found / Calculated (%) | | | | Molecular formula |
|---|---|---|---|---|---|---|---|
| | | | C | H | N | S | |
| **3a** | 47 | 229—230 | 55.01<br>55.02 | 4.65<br>4.62 | 25.65<br>25.67 | 14.65<br>14.69 | $C_{10}H_{10}N_4S$ |
| **3b** | 30 | 145—147 | 55.05<br>55.02 | 4.69<br>4.62 | 25.69<br>25.67 | 14.71<br>14.69 | $C_{10}H_{10}N_4S$ |
| **3c** | 82 | 140 | 56.87<br>56.87 | 5.21<br>5.20 | 24.14<br>24.12 | 13.80<br>13.80 | $C_{11}H_{12}N_4S$ |
| **3d** | 80 | 205—207 | 59.89<br>56.87 | 5.18<br>5.20 | 24.14<br>24.12 | 13.78<br>13.80 | $C_{11}H_{12}N_4S$ |
| **3e** | 30 | 200—202 | 61.27<br>60.28 | 6.60<br>6.61 | 20.45<br>20.42 | 11.68<br>11.69 | $C_{14}H_{18}N_4S$ |

## Experimental

Melting points were determined on a Kofler stage. The IR spectra were recorded on a UR-20 spectrophotometer (in pellets with KBr), the $^1$H NMR spectra were obtained with a Bruker WM-250 spectrometer (250 MHz) in DMSO-$d_6$, and mass spectra were obtained with a Varian MAT-313A instrument (EI, 70 eV). The elemental analysis was performed on a Perkin Elmer device. The UV spectra were obtained in EtOH with a Specord UV-VIS instrument.

**4-Alkyl-2,6-diamino-3,5-dicyano-4*H*-thiopyrans (2a—e).** Malononitrile (10 mmol), cyanothioacetamide (10 mmol), and a catalytic amount of triethylamine were added to a solution of 10 mmol of aldehyde (**1a—e**) in ethanol (10 mL). The mixture was brought to the boiling point, then cooled, and the sediment precipitated was filtered off and washed with ethanol and heptane. The yields and characteristics of compounds **2a—e** are given in Tables 1 and 2.

**4-Alkyl-6-amino-3,5-dicyanopyridine-2(1*H*)-thiones (3a—e).** A suspension of 10 mmol of thiopyrane (**2a—e**) and triethylamine (10 mmol) was boiled in ethanol for 1 h (until the mixture was dissolved completely). The cooled solution was acidified with a 10 % hydrochloric acid up to pH 1. A sediment precipitated was filtered off, washed with heptane, and recrystallized from ethanol. The characteristics of compounds **3a—e** are given in Tables 3 and 4.

**4-Alkyl-6-amino-3,5-dicyano-2-(R′-methylthio)pyridines (5a—c).** Compound **4a,d** (5 mmol) was added to a solution of the corresponding thione **3** (5 mmol) in DMF (10 mL), then a 10 % solution of KOH (5 mmol) was added dropwise with stirring. The mixture was left at 20 °C for 1—2 min and then diluted with an equal amount of water. The sediment precipitated was filtered off and recrystallized. The characteristics of compounds **5a—c** are given in Tables 5, 6.

**4-Alkyl-3,6-diamino-5-cyano-2-R′-thieno[2,3-*b*]pyridines (6).** *A.* Compound **4a—d** (5 mmol) and a 10 % solution of KOH (10 mmol, dropwise) were added to a solution of thione

**Table 4.** Spectral characteristics of 4-alkyl-6-amino-3,5-dicyanopyridine-2(1*H*)-thiones **3a—e**

| Compound | IR, νCN/cm$^{-1}$ (νCS/cm$^{-1}$) | UV, $\lambda_{max}$/nm (log ε) | Mass spectrum, *m/z* ($I_{rel}$ (%)) | $^1$H NMR, δ |
|---|---|---|---|---|
| **3a** | 2230 (1190) | 213 (6.36), 241 (6.24), 324 (6.24), 387 (6.17) | 218 (97.8), 203 (100.0), 190 (77.1), 185 (56.3), 176 (67.7), 162 (58.3), 146 (72.7), 131 (64.6) | 1.0 (t, 3 H, $CH_3$); 1.67 (m, 2 H, $CH_2$); 2.65 (t, 2 H, $CH_2$); 7.9 (br.s, 2 H, $NH_2$), 12.9 (br.s, H, NH) |
| **3b** | 2220 (1125) | | 218 (69.1), 217 (21.6), 204 (12.4), 203 (100.0); 176 (19.8); 165 (12.7), 142 (11.6); 116 (10.4), 91 (10.6), 45 (17.8) | 1.36 (d, 6 H, 2 $CH_3$); 3.21 (m, H, CH); 7.8 (br.s, 2 H, $NH_2$); 12.89 (br.s, H, NH) |
| **3c** | 2225 (1165) | 215 (5.59), 244 (5.42), 326 (5.42), 390 (5.32) | 232 (37.9), 231 (14.1), 204 (22.4), 203 (23.1), 190 (84.7), 137 (18.8), 107 (19.4), 100 (48.2) | 0.9 (t, 3 H, $CH_3$); 1.32 (m, 2 H, $CH_2$); 1.55 (m, 2 H, $CH_2$); 2.63 (t, 2 H, $\underline{CH_2}CH_3$); 7.91 (br.s, 2 H, $NH_2$); 12.9 (br.s, H, NH) |
| **3d** | 2230 (1190) | 215 (6.08), 244 (5.93), 326 (5.95), 392 (5.88) | 232 (50.9), 217 (41.8), 207 (14.2), 190 (100.0), 86 (24.2), 43 (34.2) | 0.94 (d, 6 H, 2 $CH_3$); 2.0 (m, H, CH); 2.5 (d, 2 H, $CH_2$); 7.85 (br.s, 2 H, $NH_2$); 12.86 (br.s, H, NH) |
| **3e** | 2230 (1200) | 217 (5.86), 242 (5.71), 326 (5.72), 390 (5.68) | 274 (42.2), 273 (16.3), 245 (23.3), 241 (10.1), 232 (31.3), 231 (27.2), 217 (36.7), 205 (14.9), 204 (47.6), 203 (100.0), 190 (62.7), 146 (11.7) | 0.82 (t, 3 H, $CH_3$); 1.28 (m, 8 H, $(CH_2)_4$); 1.55 (m, 2 H, $CH_2$); 2.6 (t, 2 H, $\underline{CH_2}CH_3$), 7.87 (br.s, 2 H, $NH_2$); 12.88 (br.s, H, NH) |

**Table 5.** Yields and characteristics of compounds **5a—c** and **6a—e**

| Compound | Yield (%) | M.p./°C (50 % EtOH) | Found / Calculated (%) C | H | N | S | Br | Molecular formula |
|---|---|---|---|---|---|---|---|---|
| **5a** | 68 | 203—205 | 56.67<br>56.68 | 3.92<br>3.96 | 18.35<br>18.36 | 8.40<br>8.41 | | $C_{18}H_{15}N_5O_3S$ |
| **5b** | 50 | 210—212 | 57.52<br>57.54 | 4.84<br>4.83 | 25.80<br>25.81 | 11.81<br>11.82 | | $C_{13}H_{13}N_5S$ |
| **5c** | 50 | 204—205 | 57.70<br>57.71 | 4.32<br>4.33 | 17.72<br>17.71 | 8.10<br>8.11 | | $C_{19}H_{17}N_5O_3S$ |
| **6a** | 68 | 228—229 | 53.19<br>53.20 | 4.01<br>3.99 | 13.06<br>13.06 | 7.46<br>7.47 | 18.41<br>18.63 | $C_{19}H_{17}BrN_4OS$ |
| **6b** | 65 | 260—262 | 57.69<br>57.71 | 4.34<br>4.33 | 17.70<br>17.71 | 8.12<br>8.11 | | $C_{19}H_{17}N_5O_3S$ |
| **6c** | 65 | 240—242 | 57.53<br>57.54 | 4.81<br>4.83 | 25.82<br>25.81 | 11.80<br>11.82 | | $C_{13}H_{13}N_5S$ |
| **6d** | 60 | 243—245 | 65.19<br>65.20 | 5.17<br>5.18 | 16.01<br>16.00 | 9.17<br>9.16 | | $C_{19}H_{18}N_4OS$ |
| **6e** | 70 | 175 | 67.38<br>67.40 | 6.16<br>6.17 | 14.30<br>14.29 | 8.19<br>8.18 | | $C_{22}H_{24}N_4OS$ |

**3** (5 mmol) in 10 mL of DMF or ethanol. The mixture was stirred at ~20 °C for 1—2 min and diluted with an equal amount of water. The sediment precipitated was filtered off and recrystallized.

***B.*** A 10 % solution of KOH (10 mmol) was added dropwise to a solution of pyridine **5** (5 mmol) in 10 mL of DMF or ethanol. The mixture was stirred at 20 °C for 1—2 min and diluted with an equal amount of water. The sediment precipitated was filtered off and recrystallized. The characteristics of compounds **6** are given in Tables 5 and 6.

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**Table 6.** Spectral characteristics of compounds **5a—c** and **6a—e**

| Compound | IR, νCN/cm$^{-1}$ (νCO/cm$^{-1}$) | $^1$H NMR, δ |
|---|---|---|
| **5a** | 2220 (1700) | 0.93 (t, 3 H, $CH_3$); 1.62 (m, 2 H, $CH_2$); 2.88 (t, 2 H, $\underline{CH_2}CH_3$); 4.94 (s, 2 H, $SCH_2$); 7.76 (s, 2 H, $NH_2$); 8.26 (d, 2 H, H arom.); 8.37 (d, 2 H, H arom.) |
| **5b** | 2220, 2270 | 0.9 (t, 6 H, 2 $CH_3$); 1.14 (t, 2 H, $CH_2$); 1.99 (m, H, CH); 4.28 (s, 2 H, $SCH_2$); 8.12 (s, 2 H, $NH_2$) |
| **5c** | 2220, 2237 (1700) | 0.9 (t, 6 H, 2 $CH_3$); 1.14 (t, 2 H, $CH_2$); 1.99 (m, H, CH); 4.95 (s, 2 H, $SCH_2$); 7.78 (s, 2 H, $NH_2$); 8.32 (m, 4 H, H arom.) |
| **6a** | 2225 (1680) | 0.88 (t, 3 H, $CH_3$); 1.4 (m, 2 H, $CH_2$); 1.59 (m, 2 H, $CH_2$); 3.1 (t, 2 H, $\underline{CH_2}CH_3$); 7.44 (s, 2 H, $NH_2$); 7.58 (d, 2 H, H arom.); 7.6 (d, 2 H, H arom.); 8.14 (s, 2 H, $NH_2$) |
| **6b** | 2222 (1670) | 0.9 (t, 3 H, $CH_3$); 1.4 (m, 2 H, $CH_2$); 1.6 (m, 2 H, $CH_2$); 3.14 (t, 2 H, $\underline{CH_2}CH_3$); 7.5 (s, 2 H, $NH_2$); 7.9 (d, 2 H, H arom.); 8.28 (s, 2 H, $NH_2$); 8.3 (d, 2 H, H arom.) |
| **6c** | 2209, 2238 | 0.9 (t, 3 H, $CH_3$); 1.38 (m, 2 H, $CH_2$); 1.54 (m, 2 H, $CH_2$); 3.1 (t, 2 H, $\underline{CH_2}CH_3$); 6.32 (d, 2 H, $NH_2$); 7.31 (d, 2 H, $NH_2$) |
| **6d** | 2230 (1611) | 0.95 (d, 6 H, 2 $CH_3$); 2.0 (m, H, CH); 3.08 (d, 2 H, $CH_2$); 7.48—7.55 (m, 7 H, H arom. + $NH_2$); 8.08 (s, 2 H, $NH_2$) |
| **6e** | 2230 (1630) | 0.8 (t, 3 H, $CH_3$); 1.3 (m, 8 H, $(CH_2)_4$); 1.61 (m, 2 H, $CH_2$); 3.13 (t, 2 H, $\underline{CH_2}CH_3$); 7.41—7.5 (m, 7 H, H arom. + $NH_2$); 8.1 (s, 2 H, $NH_2$) |

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